

PATENT SPECIFICATION

NO DRAWINGS



856,434

Date of Application and filing Complete Specification July 1, 1957.
No. 20758/57.

Application made in United States of America on July 12, 1956.
Application made in United States of America on Oct. 5, 1956.
Complete Specification Published Dec. 14, 1960.

Index at acceptance:—Class 2(6), P2D(1A:1B:2A), P2P(1A:1B:1C:1F:1X:3:5), P7D1X, P7P(1A:1B:1C:1F:1X:3:5).

International Classification:—C08f.

COMPLETE SPECIFICATION

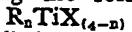
Method for Polymerizing Propylene, Butadiene, Isoprene and Chloroprene

We, NATIONAL LEAD COMPANY, a Corporation organised and existing under the Laws of the State of New Jersey, United States of America, of 111, Broadway, New York 6, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for polymerizing propylene, butadiene, isoprene and chloroprene using as catalysts organotitanium compounds having a stable carbon-titanium bond.

The invention provides a process for producing polymers from propylene, butadiene, isoprene and chloroprene which comprises admixing the hydrocarbon with a catalyst, which is an organotitanium compound containing 1 or 2 R—Ti bonds where R is an alkyl or aryl group.

The invention provides a method for producing polymers of propylene, butadiene, isoprene and chloroprene which comprises admixing the hydrocarbon with an organotitanium compound containing 1 or 2 C—Ti bonds and having the formula



where R is an alkyl, aryl, alkaryl or aralkyl group, X is an alkoxy group or halogen, and where n is 1 or 2.

The alkyl group in the catalytic compound may be varied considerably but should preferably contain from 1 to 16 carbon atoms and may be substituted or non-substituted saturated or unsaturated.

The aryl group should be a phenyl, substituted phenyl, naphthyl or substituted naphthyl group. The substituent in the substituted naphthyl or substituted phenyl groups should be lower alkoxy, lower alkyl or phenyl groups. The term "lower alkoxy"

and "lower alkyl" is meant to include those groups having from 1 to 6 carbon atoms in the hydrocarbon chain. Among those which are the most readily available are methyl, ethyl, isopropyl, butyl and cyclohexyl.

The alkoxy group, like the alkyl group, should preferably contain from 1 to 16 carbon atoms and may be substituted or non-substituted, saturated or unsaturated. The halogen substituent may be any of the halogens. It is preferred, however, to use alkoxy groups having less than 6 carbon atoms, because such groups are more reactive, and give products, in general, which are more readily isolated.

The most desirable methods for producing the catalysts are as follows:—

(1) an alkyl titanate is reacted with a metal alkyl or metal aryl compound,
(2) an alkoxytitanium halide of the form $(alkoxy)_nTi(halide)_{(4-n)}$, where n is from 0 to 4, is reacted with a metal alkyl or metal aryl, including Grignard reagents. The amounts of such reactants are chosen so that from 1 to 2 moles of arylating or alkylating reagent are reacted with 1 mole of the titanium compound. The amounts of arylating or alkylating agents employed are not in excess of those which will theoretically produce more than 1 or 2 Ti—C bonds for each titanium atom.

As stated above, the catalyst used in the invention contains 1 or 2 Ti—C bonds, and it has been discovered that when such catalysts are employed, they generate free radicals at a predetermined and reproducible rate. The exact mechanism which takes place during polymerization is not known; however, it is believed that the Ti—C bonds in such compounds undergo homolytic cleavage yielding free radicals. Using these compounds, therefore, the formation of free

[Price 3s. 6d.] 4s. 6d.

45

50

55

60

65

70

75

80

85

BEST AVAILABLE COPY

radicals takes place continuously over an extended time period, thus permitting free radicals to be released throughout the entire polymerizing reaction. The release of these free radicals results in the formation of chain initiators which provide the energy for the polymerization reaction. The role of the titanium atom in the compound is not entirely understood, but it is believed that it plays an important part in determining the molecular configuration and size of the polymer.

All of the compounds used as catalysts in the invention undergo homolytic cleavage of the Ti—C bonds at a determinable rate. The rate is controlled as follows by the various substituents on the titanium compound and by the other specified features:—

- 1) the number of R groups thus R_2 yields chain initiators faster than R_1
- 2) alkyl groups yield chain initiators faster than aryl groups
- 3) halogen yields chain initiators faster than alkoxy groups
- 4) chain initiation increases with increased temperature
- 5) solvent variations.

It is, therefore, possible to select catalysts containing 1 or 2 Ti—C bonds according to the invention, which will undergo homolytic cleavage at room temperature over a considerable range of time periods; for example, in a matter of minutes in the case of a dialkyl titanium dihalide, to several weeks in the case of an aryltitanium trialkoxide.

Many of these catalysts are soluble in the solvents used for carrying out the polymerization reaction and, therefore, effective and efficient homogeneous reaction systems are obtained.

The catalysts used for polymerization in the invention are simple to prepare. The reactants are merely mixed together and either used immediately as polymerization agents or are separated from the reactant products and stored until their use is desired.

The catalysts of the invention are highly efficient and, therefore, the polymerization reactions may be carried out in the presence of small amounts of catalysts. Since these catalysts are simple compounds instead of being complex mixtures containing excessive quantities of inactive reactants, the used catalyst of the invention is more easily removed from the polymer formed.

In carrying out the polymerization according to the invention, the catalyst may be used alone or in conjunction with a solvent. Many solvents may be employed for this purpose. Among these are included hexane, cyclohexane, benzene, toluene, n-heptane and xylene. The reaction, in some instances, may be carried out at room temperature; however, it has been found, in general, that

the polymer forms more readily at temperatures somewhat higher than room temperature. At the end of the reaction the polymer formed in the vessel is removed and washed to remove the solvent and reaction by-products.

Following is a description by way of example of methods of carrying the invention into effect.

EXAMPLE 1

Dimethyltitanium dichloride was used as the catalyst for the polymerization of propylene. Dimethyltitanium dichloride containing 2 Ti—C bonds was prepared by mixing 0.04 mole of titanium tetrachloride with 0.08 mole of methyl magnesium iodide in 50 ml. of ether. 0.036 mole of the catalyst was added to 150 ml. of n-hexane and was charged to an autoclave together with 250 ml. of liquid propylene. The sealed autoclave was heated and agitated at a temperature of 150° C. over an 8 hour period. The bomb was opened, the polypropylene was removed and washed. The polypropylene was a white, linear, highly crystalline, macromolecular polymer. It did not soften at temperatures up to 175° C. and was essentially insoluble in boiling tetrahydronaphthalene.

EXAMPLE 2

Isopropyltitanium tributoxide was used as the catalyst for polymerizing propylene. The catalyst was prepared by mixing 1 mole of isopropyl magnesium chloride with 1 mole of tetrabutyl titanate. 0.04 mole of the catalyst was dissolved in n-heptane. This was placed in the autoclave together with 250 ml. of liquid propylene. The sealed autoclave was heated and agitated at 130° C. overnight. The bomb was opened, and the polypropylene was removed and washed. The polypropylene was a white, linear, highly crystalline, macromolecular polymer which did not melt at temperatures up to 200° C. and was essentially insoluble in boiling tetrahydronaphthalene.

The above examples clearly show that a superior type of polypropylene has been produced which is characterized by a melting range above 150° C. and is insoluble and non-reactive in tetrahydronaphthalene at temperatures up to 150° C. The polypropylene produced is linear, crystalline and macromolecular.

EXAMPLE 3

Phenyltitanium triisopropoxide was used as the catalyst for polymerizing butadiene. Phenyl magnesium bromide was mixed with tetrabutyl titanate on a mole for mole basis in ether to prepare 0.034 mole of phenyltitanium triisopropoxide which contained 1 Ti—C bond. The catalyst was dissolved in 150 ml. of cyclohexane and charged to an

BEST AVAILABLE COPY

autoclave together with 250 ml. of liquid butadiene. The sealed autoclave was heated and agitated to a temperature of 100° C. over a five hour period. The bomb was opened, the polybutadiene was removed and washed. The polybutadiene was a white, crystalline, macromolecular polymer. It did not melt at temperatures up to 150° C.

- EXAMPLE 4
- 10 Diphenyltitanium dibutoxide was used as the catalyst for polymerizing isoprene. This catalyst was prepared by mixing 2 moles of phenyl magnesium bromide with 1 mole of tetrabutyl titanate. In carrying out the polymerization of isoprene, 0.04 mole of diphenyltitanium dibutoxide was added to 150 ml. of cyclohexane. This was placed in the autoclave together with 250 ml. of isoprene. The sealed autoclave was heated with agitation to 50° C. over a seven hour period. The bomb was opened, the polyisoprene was removed and washed. The polyisoprene was white, crystalline, macromolecular polymer and was highly resistant to dissolution in organic solvents.

- EXAMPLE 5
- 15 Diphenyltitanium dibutoxide was used as the catalyst for polymerizing chloroprene. This catalyst was prepared by mixing 2 moles of phenyl magnesium bromide with 1 mole of tetrabutyl titanate. In carrying out the polymerization of chloroprene, 0.04 mole of diphenyltitanium dibutoxide was dissolved in 150 ml. of xylene. This was placed in an autoclave together with 250 ml. of chloroprene. The sealed autoclave was heated and agitated to a temperature of 130° C. over an eight hour period. The bomb was opened, the polychloroprene was removed and

washed. The polychloroprene was white, crystalline, macromolecular polymer and highly resistant to dissolution in organic solvents.

40 From the above description and by the examples presented, it has clearly been shown that polymers may be produced using the specified organotitanium catalysts containing 1 or 2 Ti—C bonds.

45 WHAT WE CLAIM IS:—

50 1. A method for producing polymers of propylene, butadiene, isoprene and chloroprene which comprises admixing the hydrocarbon with an organotitanium compound containing 1 or 2 C—Ti bonds and having the formula



55 where R is an alkyl, aryl, alkaryl or aralkyl group, X is an alkoxy group or halogen, and n is 1 or 2.

60 2. A method as claimed in Claim 1 wherein R is an alkyl group containing from 1 to 16 carbon atoms, or a phenyl, substituted phenyl, naphthyl or substituted naphthyl group wherein the substituents of the substituted phenyl and naphthyl groups are lower alkoxy or lower alkyl groups having from 1 to 6 carbon atoms in the hydrocarbon chain, or wherein the substituents are phenyl groups.

65 3. A method as claimed in Claim 1 or Claim 2, wherein X is an alkoxy group containing from 1 to 16 carbon atoms.

70 4. A method for producing polymers of propylene, butadiene, isoprene and chloroprene substantially as described with reference to any one of the specific examples hereinbefore set forth.

75 BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1960.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained

BEST AVAILABLE COPY

THIS PAGE BLANK (USPTO)